PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : B01J 13/10	A1	(11) International Publication Number: WO 99/17871
		(43) International Publication Date: 15 April 1999 (15.04.99)

(21) International Application Number: PCT/IB98/01551

(22) International Filing Date: 5 October 1998 (05.10.98)

(30) Priority Data:
08/947,694 8 October 1997 (08.10.97) US

(71) Applicant: GIVAUDAN ROURE (INTERNATIONAL) S.A. [CH/CH]; 5, chemin de la Parfumerie, CH-1214 Vernier (CH).

(71)(72) Applicant and Inventor *(for AT BE CH CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE only)*: SOPER, Jon, C. [US/US]; 1037 Mulford Road, Lebanon, OH 45036 (US).

(72) Inventors: KIM, Young, D.; 8855 Steeplechase Way, West Chester, OH 45069 (US). THOMAS, Margaret, T.; 832 Revere Village Court, Centerville, OH 45069 (US).

(74) Agents: JOSEPHIC, David, J._ et al.; Wood, Herron & Evans, L.L.P., 2700 Carew Tower, Cincinnati, OH 45202 (US).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: METHOD OF ENCAPSULATED FLAVORS AND FRAGRANCES BY CONTROLLED WATER TRANSPORT INTO MICROCAPSULES

(57) Abstract

A method of encapsulating an amphiphilic flavor or fragrance compound into a microcapsule having a hydrogel shell and an oil core. The flavor or fragrance compound is transported into and solubilized in the core by partition coefficient equilibrium using water in the capsule wall to transport the compound into the core. Microcapsules made by the method of the invention may have a wall thickness and contain a high concentration of the flavor or fragrance compound that has not previously been feasible.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

METHOD OF ENCAPSULATING FLAVORS AND FRAGRANCES BY CONTROLLED WATER TRANSPORT INTO MICROCAPSULES

FIELD OF THE INVENTION

This invention relates to a method of encapsulating flavors or fragrances into microcapsules having a hydrogel shell and an oil core.

BACKGROUND OF THE INVENTION

Microcapsules incorporating a flavor or fragrance compound are useful to provide a controlled release of the contained flavor or fragrance. Such products may be used in the food processing industry, where encapsulated flavor particles may provide a flavor burst upon chewing the food. Such products may also be used in the cosmetic and toiletry industries, where encapsulated fragrance particles may provide a burst of scent upon capsule fracture. The capsule may comprise a shell surrounding a core material in which the flavor or fragrance compound is contained.

Microcapsules may be formed by a coacervation or crosslinking process, in which lipids are coated by tiny droplets of proteins, carbohydrates, or synthetic polymers suspended in water.

The process of coacervation is, however, difficult to control and depends on variables such as temperature, pH, agitation of the materials, and the inherent variability introduced by a natural protein or carbohydrate.

In the manufacture of microcapsules containing a flavor or fragrance compound, several features are desirable. It is desirable to produce microcapsules that have strong walls and that do not agglomerate. It is desirable that the compound be readily loaded into an oil microparticle, that is, be readily absorbed into the oil core of the microcapsule. Once absorbed, it is also desirable that the compound be irreversibly retained in the oil core of the microcapsule, that is, be adsorbed into the microcapsule.

The amount of compound that may be encapsulated depends upon several factors including its solubility in water, partition coefficient, molecular weight, water content, volatility, and the ratio of blank capsule to water amounts. Flavors and fragrances may be mixtures of hundreds of components, each of which may widely in these properties. A flavor or fragrance compound that is lipophilic may be readily contained in an oil core of a microcapsule, while a flavor or fragrance compound that is hydrophilic may be less readily contained in an oil core. For example, the flavor compound diacetyl (DA) is about 20% to about 30% water soluble. For diacetyl, typical maximum absorption into an oil is up to only about 55%. A highly water soluble

compound such as diacetyl is also more difficult to retain in the oil core once it is loaded.

A compound's solubility in an aqueous phase versus an oil phase is determined by its partition coefficient, abbreviated as K. The partition coefficient of a compound is the ratio of the compound's concentration in one liquid phase to the compound's concentration in another liquid phase. The partition coefficient thus is an inherent property of the compound with two given liquid phases, such as a lipid phase and an aqueous phase, and reflects the compound's distribution at equilibrium between the water phase and the lipid phase. Any means of decreasing the water solubility of a compound will shift the equilibrium of the compound and thus shift its partitioning between an aqueous phase and a lipid phase. For example, addition of a salt will decrease the water solubility of a compound and will increase its partitioning into the lipid phase. Similarly, crosslinking a protein membrane to strengthen the membrane and physically decrease the amount of water, or physically removing water from the environment, causing capsule wall or membrane shrinking, will decrease the water solubility of a compound and will increase its partitioning into the oil phase.

Flavors or fragrances that are water soluble may interfere with encapsulation of an oil particle. For example, flavor or fragrance compounds that are water soluble cannot be encapsulated using gelatin

coacervation. This is because for coacervation to occur, there must be a droplet to coat, and for these water soluble materials, there are no droplets to coat. In addition, the water soluble flavor or fragrance may partition so as to locate the flavor or fragrance compound in an aqueous environment outside the encapsulated oil particle rather than inside the oil particle. If a flavor or fragrance compound is too water soluble, the coacervation process ceases to function due to the colloid becoming either too thick or too thin. A colloid that is too thick has no flow, and thus cannot properly coat the oil surface. A colloid that is too thin is not retained on the oil surface. In the extreme, a water soluble flavor or fragrance compound can totally solubilize the colloid, leaving no wall material to deposit on the oil surface.

Besides water solubility, a flavor or fragrance compound that contains fatty acids affects the pH of a coacervation reaction. If a base is added in an attempt to adjust pH, the fatty salts produced in the reaction impart an undesirable soap taste to a flavor compound. If a flavor or fragrance compound contains water soluble esters, the coacervation temperature is affected and hence the final gelation temperature is altered. While it is therefore desirable to limit compounds that contain either fatty acids or water soluble esters, there is a tradeoff in the potency and profile results for the encapsulated compound. This limits the range of formulations that are able to be effectively encapsulated.

Currently, flavor or fragrance compounds that are difficult to encapsulate are diluted with oils such as vegetable oil or mineral oil. This alters its oil to water partition coefficient, in which the compound attempts to reach an equilibrium between the oil and aqueous phases. The oil serves to reduce the natural water solubility of most compounds and, in many cases, reduces it below the level at which it interferes with coacervation. A flavor or fragrance compound that is highly water soluble, however, does not have this effect. A compound that has a water solubility greater than 25% prefers to partition in an aqueous phase, and a ratio of lipid:water greater than 90% is needed to encapsulate these compounds. The coacervation process, however, is generally limited to about 22% lipid. Thus, this technique is of only limited applicability for water soluble flavor or fragrance compounds.

Several techniques are known in the art for absorbing compounds into a microcapsule, such as cyclodextrin entrapment or silica plating. A drawback of the cyclodextrin entrapment technique is that the binding effect varies widely depending upon the particular flavor or fragrance compound. A drawback of the silica plating technique is that there is no barrier to protect the flavor or fragrance compound from evaporation. Thus, there is a need for an efficient method of absorbing the many types of flavor and fragrance compounds to the desired level of loading in an encapsulated oil. There

is also a need for an efficient method of adsorbing flavor and fragrance compounds once they have been encapsulated.

SUMMARY OF THE INVENTION

This invention relates to a method of encapsulating a flavor or fragrance compound by controlled water transport of the compound into a capsule having an oil core. The method comprises preparing a microcapsule having a hydrogel shell and an oil core, and thereafter adding an amphiphilic flavor or fragrance compound in the presence of water to the microcapsule to transport the compound through the hydrogel shell and into the oil core. The compound is transported into the core by aqueous diffusion through the hydrogel shell. The oil core is retained in the hydrogel shell during the aqueous diffusion. A flavor or fragrance compound is thus encapsulated in the hydrogel shell containing the retained oil core.

The shell may consist of a carbohydrate or a protein, which may be crosslinked or non-crosslinked, or a synthetic polymer such as polyvinyl pyrollidone or methyl cellulose. The oil core may comprise, for example, vegetable oil, mineral oil, benzyl alcohol, or mixtures thereof. In a preferred embodiment, the oil is a short chain triglyceride of fractionated coconut oil. As more particularly defined hereinafter, "oil" is meant to include a wide range of substances that are dispersible in water due to their hydrophobic nature.

In an alternative embodiment of the invention, the microcapsule may be prepared in a dry form. An amphiphilic flavor or fragrance compound is added, in the presence of a controlled volume of water, to a substantially dry microcapsule having a hydrogel shell surrounding an oil core. The compound is transported through the hydrogel shell by aqueous diffusion into the oil core and is retained in the core. The microcapsule having the flavor or fragrance compound retained in the oil core is then dried.

In a preferred form of the invention, a flavor or fragrance compound is encapsulated by preparing a microcapsule of a coacervate of an oil core and a hydrogel shell, adding the flavor or fragrance compound in the presence of water to the microcapsule for transportation of the compound into the oil core, transporting the compound through the hydrogel shell by aqueous diffusion, and retaining the oil core in the hydrogel shell during the transportation to provide the encapsulated flavor or fragrance and retained oil core in the hydrogel shell.

The invention is also directed to the products produced by the methods of the invention.

One advantage of the invention is that the microcapsule may contain a concentration of the flavor or fragrance compound that heretofore has not been feasible. A second advantage is that the walls of the blank microcapsules have a substantially uniform thickness,

strength, and resiliency. Another advantage is the increased yield of encapsulated flavor or fragrance, since essentially no flavor or fragrance compound is lost to the environment. Still another advantage is the economy in manufacturing the flavor or fragrance compounds of the invention, since the same technology is used for all flavors and fragrances.

The objectives and other advantages of this invention will be further understood with reference to the following detailed description and examples.

DETAILED DESCRIPTION

In a preferred practice of the invention, microcapsules containing a desired flavor or fragrance compound are formed by a coacervation process. In coacervation, there is separation of a colloid into a colloid-rich phase (the coacervate) and an aqueous solution of the coacervating agent (the equilibrium liquid), forming an oil coated with protein, carbohydrate, or polymeric droplets so as to suspend the oil in water. In the process, two lipid phases and one aqueous phase are ultimately absorbed into one lipid phase and one aqueous phase. The first lipid phase forms the microcapsule core. The core is surrounded by a hydrogel capsule, defined herein as a colloid in which the dispersed phase (colloid) has combined with the continuous phase (water) to produce a viscous jellylike product. The core consists of an oil which is a term used herein to define a wide range of substances

that are quite different in their chemical nature. Oils may be classified by their type and function and encompass mineral oils (petroleum or petroleum-derived), vegetable oils (chiefly from seeds and nuts), animal oils (usually occurring as fats; the liquid types include fish oils), essential oils (complex volatile liquids derived from flowers, stems, leaves, and often the entire plant), and edible oils (chiefly vegetable oils as well as some special fish oils). Oils derived from living organisms are chemically identical with fats, the only difference being one of consistency at room temperature. In one embodiment, the oil may be mineral oil, vegetable oil, or benzyl alcohol. In a preferred embodiment, the oil is a short chain triglyceride of fractionated coconut oil, available under the tradenames Migylol® (Huls Corp., Piscataway, NJ) or Captex® (Abitec Corp., Janesville, WI). The hydrogel shell may be either carbohydrate, protein, or a synthetic polymer such as polyvinyl pyrollidone or methyl cellulose. In a preferred embodiment, the oil is Migylol® or Captex® and the shell is gelatin. The second lipid phase is the desired flavor or fragrance compound, which is to some extent both water-soluble and lipid-soluble, that is, it is amphiphilic, which is the term used herein to define its dual solubility properties. The aqueous phase is used to transport, by partition coefficient equilibrium, the slightly water soluble flavor or fragrance compound into the oil core of the microcapsule by aqueous diffusion. Equilibrium dynamics continue

until the three phases (two lipid and one aqueous) are absorbed into two phases (one lipid and one aqueous).

For some water soluble compounds, less water is required for absorption or partitioning into the oil phase. Conversely, for some highly lipid soluble compounds, more water may be required for partitioning into the oil phase. Thus, by transiently varying the amount of water that is available to a compound, taking into account the compound's partition coefficient, a compound may be absorbed through the hydrogel shell into an oil.

Adsorption of the compound in the oil can be controlled. Dehydration of the microcapsule or crosslinking of the capsule shell locks the flavor or fragrance compound inside the microcapsule. In dehydration, a substantial volume of the water is removed from the capsule, thereby reducing the loss of the partially water-soluble flavor or fragrance compound from the oil core into an aqueous environment. Alternatively, crosslinking of the hydrogel shell of the coacervate renders the encapsulated oil thermostable, since a capsule containing crosslinks is a stable structure. The use of known chemical crosslinking agents, such as formaldehyde or glutaraldehyde, to irreversibly crosslink the oil-containing capsule is known.. Other crosslinking agents such as tannic acid (tannin) or potassium aluminum sulfate (alum) are similarly known. An optional capsule hardening step, as disclosed in U.S. Patents no. 2,800,457 and 2,800,458, consists of

adjusting a suspension of capsular material to pH 9 to 11, cooling to 0°C to 5°C, and adding formaldehyde. Formaldehyde and glutaraldehyde are also effective chemical crosslinking agents. For the food industry and the cosmetic/toiletry industries, suitable cross-linking agents may be selected depending upon the specific application.

Certain naturally-occurring enzymes are also good cross-linking agents. Crosslinking using enzymes, such as transglutaminase, is disclosed in co-pending application Serial No. 08/791,953 entitled Enzymatically Protein-Encapsulating Oil Particles by Complex Coacervation, which is hereby incorporated by reference in its entirety. Enzymes work by catalyzing the formation of bonds between certain amino acid side chains in proteins. In addition, because the enzymes are naturally occurring, encapsulated oils that are enzymatically crosslinked do not suffer from the problems inherent with formaldehyde and glutaraldehyde crosslinking, and hence may be ingested or applied without the concern of toxicity of the crosslinking agent. Because crosslinking is a enzyme catalyzed reaction, however, the proper environmental conditions must exist for optimum enzyme activity.

For compounds with high water solubility, defined herein as at least about 20% water soluble, it is preferable to concentrate the microcapsule to 55% solids or to start with dry microcapsules and gravimetrically add water and compound to get the desired results. For

compounds with low water solubility, defined herein as less than about 20% water soluble, a hydrated microcapsule preparation may be used.

EXAMPLE 1

Blank capsules that are hydrated are prepared by pre-warming deionized water to 50°C ± 2°C. A gum solution is prepared by vigorously agitating prewarmed deionized water (87.2018 g), carboxymethyl cellulose, sodium salt (1.8447 g), and gum arabic FCC powder SP Dri (0.1845 g). The solution is mixed until the solids are completely dissolved, then the solution is cooled to about 35°C to about 40°C. A gelatin solution is prepared by vigorously agitating prewarmed deionized water (163.0453 g) and 250 Bloom type A gelatin (18.4461 g) in a preemulsion tank until the gelatin is completely dissolved, then the solution is cooled to about 35°C to about 40°C. Without agitation, the gum solution is added to the gelatin solution in the preemulsion tank and the foam is allowed to dissipate for about 15-20 min. The pH is adjusted to about 5.5 with either a dilute sodium hydroxide solution (50% w/w) or a dilute citric acid solution (50% w/w).

Vegetable oil (180.02 g of Captex® 355 mixed triglycerides or Migylol®) is added with slow agitation, avoiding pooling of the oil. The capsule size is adjusted to about 100 microns to about

400 microns and the size is verified microscopically. The solution is slowly cooled at about 1°C per 5 min until the solution reaches about 28°C. If the capsule walls are intact, as determined by microscopic examination of capsules showing uniform deposition of protein with no free protein floating in the water phase, the solution may be quickly cooled to about 10°C. If the capsule walls are thin, as determined by microscopic examination of capsules showing nonuniform deposition of protein and free protein floating in the water phase, the solution is reheated to about 32°C to about 33°C. The solution is mixed at about 5°C to about 10°C for 1 h. The solution is then heated to about 15°C to about 20°C. Fifty percent glutaraldehyde is added and allowed to mix for about 16 h. Agitation is then discontinued and the capsules are allowed to separate by flotation. Approximately 48% to 50% (approximately 379 lbs to 395 lbs) of water is drained from the bottom of the tank into a separate vessel. If capsules are present in the drained liquid, draining is stopped and agitation is begun to resuspend the separated capsules into solution. The separation step is then repeated. Once separation is complete, agitation is again begun in order to resuspend the capsules into solution. Sodium benzoate (10% w/w) is added with thorough mixing. If necessary, citric acid is added to adjust the pH to less than 4.0.

Blank capsules, defined herein as encapsulated oil with no flavor or fragrance value, that are dry are prepared by the following

method. A syloid solution is prepared by mixing a silica compound syloid 244 grade 68 powder (15.9497 g) with deionized water (143.5477 g) until the powder is completely dispersed and no lumps are present. The flavor is mechanically mixed until smooth, then the syloid solution is mixed with the flavor until it is completely dispersed with no lumps, thinning out after about 30 min of stirring. The product is concentrated by centrifugation to about 50% or more solids. The material is then dried in either a vacuum oven dryer at about 80°C or in a fluid bed dryer at about 70°C.

The dry crosslinked capsules (400 g) are placed in a stainless steel mixing bowl (Hobart Lab Scale Mixer). The desired neat flavor (428.6 g) is mixed with deionized water (171.4 g) on a magnetic stirrer for 5 min. The dry capsules are mixed with the water/flavor mixture on the Hobart Mixer at power level 1-2 for 5 min. The mixture is poured into a plastic storage container, using a rubber spatula to scrap the sides of the mixing bowl, and the container is closed. The mixture is allowed to incubate for 24 h for flavor absorption before the product is used.

EXAMPLE 2

Blank capsules that are hydrated are prepared by pre-warming deionized water to 50°C ± 2°C. A gum solution is prepared by vigorously agitating prewarmed deionized water (87.2018 g), carboxymethyl cellulose, sodium salt (1.8447 g), and gum arabic FCC

powder SP Dri (0.1845 g). The solution is mixed until the solids are completely dissolved, then the solution is cooled to about 35°C to about 40°C. A gelatin solution is prepared by vigorously agitating prewarmed deionized water (163.0453 g) and 250 Bloom type A gelatin (18.4461 g) in a preemulsion tank until the gelatin is completely dissolved, then the solution is cooled to about 35°C to about 40°C. Without agitation, the gum solution is added to the gelatin solution in the preemulsion tank and the foam is allowed to dissipate for about 15-20 min. The pH is adjusted to about 5.5 with either a dilute sodium hydroxide solution (50% w/w) or a dilute citric acid solution (50% w/w).

Vegetable oil (180.02 g of Captex® 355 mixed triglycerides or Migylol®) is added with slow agitation, avoiding pooling of the oil. The capsule size is adjusted to about 100 microns to about 400 microns and the size is verified microscopically. The solution is slowly cooled at about 1°C per 5 min until the solution reaches about 28°C. If the capsule walls are intact, as determined by microscopic examination of capsules showing uniform deposition of protein with no free protein floating in the water phase, the solution may be quickly cooled to about 10°C. If the capsule walls are thin, as determined by microscopic examination of the capsules showing nonuniform protein deposition and free protein in the water phase, the solution is reheated to about 32°C to about 33°C. The solution is mixed at about 5°C to

about 10°C for 16 h, then agitation is discontinued and the capsules are allowed to separate by flotation. Approximately 48% to 50% (approximately 379 lbs to 395 lbs) of water is drained from the bottom of the tank into a separate vessel. If capsules are present in the drained liquid, draining is stopped and agitation is begun to resuspend the separated capsules into solution. The separation step is then repeated. Once separation is complete, agitation is again begun in order to resuspend the capsules into solution. Sodium benzoate (10% w/w) is added with thorough mixing. If necessary, citric acid is added to adjust the pH to less than 4.0. The capsules are stored at about 5°C to about 10°C.

The hydrated uncrosslinked beads (815.20 g) are added to a glass reactor at about 5°C to about 10°C. Stirring at about 95-100 rpm is begun while maintaining the temperature at about 5°C to about 10°C. Neat flavor or fragrance (181.8 g) is added to the glass reactor. The mixture is stirred for about 2 h at about 5°C to about 10°C to allow the flavor or fragrance to absorb into the capsules. Fifty percent glutaraldehyde (3.0 g) is then added and allowed to mix at about 15°C to about 20°C for 16 h. Sodium benzoate (10.25 g of a 10% solution) is added to the reactor. Citric acid (20%) is added to adjust the pH of the solution to 3.9. The capsules are stabilized by adding a well-mixed xanthan gum/propylene glycol mixture (1 part xanthan to 2 parts propylene glycol). The mixture is stirred for about

30 min until the capsules are stabilized. Once the capsules are stabilized, they are ready for use.

EXAMPLE 3

Sodium alginate (8.22 g, type FD 155, Grinsted Corp.) was dissolved in deionized water (300 g). The solution was stirred until homogeneous. Microcapsules (3.75 g) were added with stirring until a homogeneous phase formed. Miglyol® (99.9 g) was then added with vigorous stirring to form an oil-in-water emulsion. The emulsion was fed through a vibrating needle (1.22 mm internal diameter) that was positioned about one inch above the lowest point of an eddy generated in a glass beaker by vigorous stirring of a 4% w/w aqueous $CaCl_2$ solution (150 ml). The flow rate of the emulsion through the needle was adjusted to prevent formation of a jet. Emulsion droplets, upon entering the $CaCl_2$ solution, immediately gelled, yielding particles of about 800 μm diameter. After the emulsion was added, the slurry of beads was permitted to stand for about 30 min to allow migration of calcium ions into the microcapsules. The microcapsules were dewatered at room temperature either by centrifugation or by vacuum filtration, and were subsequently dried by techniques known in the art such as vacuum oven drying or fluid bed drying.

The resulting microcapsules had a slight tendency to stick together due to the presence of some surface oil. A free-flowing, dry alginate-encapsulated flavor or fragrance compound was obtained by

mixing the microcapsules (about 58%) and water (about 7%) with the desired flavor or fragrance compound (about 35%). The optimal absorption time is between about one hour and ten hours, depending upon the partition coefficient of the particular flavor or fragrance compound.

It should be understood that the embodiments of the present invention shown and described in the specification are only preferred embodiments of the inventors who are skilled in the art and are not limiting in any way. Therefore, various changes, modifications or alterations to these embodiments may be made or resorted to without departing from the spirit of the invention and the scope of the following claims.

What is claimed is:

1. A method of making an encapsulated flavor or fragrance compound comprising:

preparing a microcapsule having a hydrogel shell surrounding an oil core,

adding an amphiphilic flavor or fragrance compound in the presence of water to the microcapsule for transportation of the compound into the oil core,

transporting the compound by aqueous diffusion through the hydrogel shell into the oil core, and

retaining the oil core in the hydrogel shell during said transportation to provide the encapsulated flavor or fragrance in the hydrogel shell containing the retained oil core.

2. The method of claim 1 wherein the microcapsule is dried before adding the flavor or fragrance compound in the presence of water.

3. The method of claim 1 wherein the shell is selected from the group consisting of a protein, a carbohydrate, and a synthetic polymer.

4. The method of claim 3 wherein the synthetic polymer is polyvinyl pyrollidone.

5. The method of claim 1 wherein the oil core is selected from the group consisting of a mineral oil, a vegetable oil, a benzyl alcohol, and mixtures thereof.

6. The method of claim 5 wherein the vegetable oil is a short chain triglyceride of fractionated coconut oil.

7. The method of claim 1 further comprising treating the shell to prevent removal of the flavor or fragrance compound from the microcapsule.

8. The method of claim 7 wherein the treating is by removing water from the shell.

9. The method of claim 8 wherein the removing water is by adding a salt.

10. The method of claim 7 wherein the treating is by crosslinking the shell.

11. The method of claim 10 wherein the crosslinking is by adding a crosslinking agent.

12. The method of claim 10 wherein the crosslinking is performed before the flavor or fragrance compound is added to the microcapsule.

13. The method of claim 10 wherein the crosslinking is performed after the flavor or fragrance compound is added to the microcapsule.

14. The method of claim 1 wherein the microcapsule is prepared by coacervation of an oil core and a hydrogel shell.

15. The method of claim 1 wherein a mixture of flavor or fragrance compounds is added to the microcapsule.

16. A product of the method of claim 1.

17. A product of the method of claim 3.

18. A product of the method of claim 5.

19. A product of the method of claim 6.

20. A product of the method of claim 14.

21. A method of making an encapsulated flavor or fragrance compound comprising:

preparing a substantially dry microcapsule having a hydrogel shell surrounding an oil core,

adding an amphiphilic flavor or fragrance compound in the presence of a controlled volume of water to the microcapsule for transportation of the compound into the oil core,

transporting the compound by aqueous diffusion through the hydrogel shell into the oil core,

retaining the oil core in the hydrogel shell during the transportation to provide the encapsulated flavor or fragrance in the hydrogel shell containing the retained oil core, and

drying the microcapsule having the flavor or fragrance compound retained in the oil core.

22. The method of claim 21 wherein the shell is selected from the group consisting of a protein, a carbohydrate, and a synthetic polymer.

23. The method of claim 22 wherein the synthetic polymer is polyvinyl pyrollidone.

24. The method of claim 21 wherein the oil core is selected from the group consisting of a mineral oil, a vegetable oil, a benzyl alcohol, and mixtures thereof.

25. The method of claim 24 wherein the vegetable oil is a short chain triglyceride of fractionated coconut oil.

26. The method of claim 21 further comprising treating the shell to prevent removal of the flavor or fragrance compound from the microcapsule.

27. The method of claim 26 wherein the treating is by crosslinking the shell.

28. The method of claim 27 wherein the crosslinking is by adding a crosslinking agent.

29. The method of claim 27 wherein the crosslinking is performed before the flavor or fragrance compound is added to the microcapsule.

30. The method of claim 27 wherein the crosslinking is performed after the flavor or fragrance compound is added to the microcapsule.

31. The method of claim 21 wherein the microcapsule is prepared by coacervation of an oil core and a hydrogel shell.

32. The method of claim 21 wherein a mixture of flavor or fragrance compounds is added to the microcapsule.

33. A product of the method of claim 21.

34. A product of the method of claim 22.

35. A product of the method of claim 24.

36. A product of the method of claim 25.

37. A product of the method of claim 31.

38. A method of making an encapsulated flavor or fragrance compound comprising:

preparing a microcapsule by coacervation of an oil core in a hydrogel shell,

adding an amphiphilic flavor or fragrance compound in the presence of water to the microcapsule for transportation of the compound into the oil core,

transporting the compound by aqueous diffusion through the hydrogel shell into the core, and

retaining the oil core in the hydrogel shell during said transportation to provide the encapsulated flavor or fragrance in the hydrogel shell containing the retained oil core.

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01J13/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 096, no. 002, 29 February 1996 & JP 07 275688 A (KYOWA YAKUHIN KOGYO), 24 October 1995 see abstract ---	
A	DATABASE WPI Section Ch, Week 950225 October 1994 Derwent Publications Ltd., London, GB; Class A,Page 14, AN 95-010988 XP002086111 & JP 06 296856 A (KYOWA YAKUHIN KOGYO) , 25 October 1994 see abstract --- -/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
30 November 1998	09/12/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Fouquier, J-P

Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication where appropriate, of the relevant passages	Relevant to claim No
A	DATABASE WPI Section Ch, Week 853015 June 1985 Derwent Publications Ltd., London, GB; Class A,Page 96, AN 85-181439 XP002086112 & JP 60 110331 A (AGENCY OF IND. SCI. &TECHNOLOGY), 15 June 1985 see abstract	
A	DATABASE WPI Section Ch, Week 853015 June 1985 Derwent Publications Ltd., London, GB; Class A,Page 96, AN 85-181438 XP002086113 & JP 60 110330 A (AGENCY OF IND. SCI. & TECHNOLOGY), 15 June 1985 see abstract	
A	WO 93 19621 A (TASTEMAKER) 14 October 1993 see claims 1-28	

1

INTERNATIONAL SEARCH REPORT

In ational Application No
PCT/IB 98/01551

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9319621 A	14-10-1993	AT 129855 T	15-11-1995
		AU 3969893 A	08-11-1993
		BR 9306153 A	30-06-1998
		CA 2130442 A,C	14-10-1993
		CZ 9402365 A	17-05-1995
		DE 69300768 D	14-12-1995
		DE 69300768 T	05-06-1996
		DK 633732 T	26-02-1996
		EP 0633732 A	18-01-1995
		ES 2081214 T	16-02-1996
		FI 944517 A	29-09-1994
		JP 8501441 T	20-02-1996
		NZ 251818 A	28-05-1996
		RU 2089077 C	10-09-1997
		SK 114994 A	05-01-1995
		US 5536513 A	16-07-1996
		US 5759599 A	02-06-1998